

REPORT DOCUMENTATION PAGE			1 Form Approved OMB NO. 0704-0188	
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			5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS Ariel Ismach, Harry Chou and Rodney S. Ruoff			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Texas at Austin 101 East 27th Street Suite 5.300 Austin, TX 78712 -1539			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
14. ABSTRACT The large-area growth of hexagonal boron nitride (h-BN) with controllable thickness (number of layers) and down to the 1-2 layers was demonstrated. In addition to the standard characterization tools used for h-BN films, such as, scanning and transmission electron microscopies (SEM and TEM), Raman spectroscopy and mapping and x-ray photoelectron spectroscopy (XPS), other less common methodologies were used as well. For example, low energy electron microscopy and diffraction was found to provide large-area and accurate number of layers; Time of flight secondary ion mass spectroscopy (TOF SIMS) provided with a 2D mapping of elements and photoluminescence				
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				19a. NAME OF RESPONSIBLE PERSON Rodney Ruoff
				19b. TELEPHONE NUMBER 512-471-4691

Report Title

Synthesis and Characterization of Hexagonal Boron Nitride (h-BN) Films.

ABSTRACT

The large-area growth of hexagonal boron nitride (h-BN) with controllable thickness (number of layers) and down to the 1-2 layers was demonstrated. In addition to the standard characterization tools used for h-BN films, such as, scanning and transmission electron microscopies (SEM and TEM), Raman spectroscopy and mapping and x-ray photoelectron spectroscopy (XPS), other less common methodologies were used as well. For example; low energy electron microscopy and diffraction was found to provide large-area and accurate number of layers; Time of flight secondary ion mass spectroscopy (TOF-SIMS) provided with a 3D mapping of elements and photoluminescence (PL) measurements were detected even from a 1-2 layers on top of a thin graphite layer, and thus, proving the presence of the h-BN phase on top of the graphene/graphite when being very challenging to do so by means of other methodologies. These results allowed us to study in better detail the growth mechanism and few manuscripts are in preparation. We believe our work will lead to a better understanding of the h-BN growth process and thus pave the way to a wide variety of applications.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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01/09/2014	4.00 Sheneve Z. Butler, [†] , Shawna M. Hollen, [‡] , Linyou Cao, [§] Yi Cui, [^] Jay A. Gupta, [‡] Humberto R. Gutierrez, ⁰ , Tony F. Heinz, [,] Seung Sae Hong, [^] Jiaying Huang, ^z Ariel F. Ismach, [#] Ezekiel Johnston-Halperin, [‡] , Masaru Kuno, ⁴ Vladimir V. Plashnitsa, ⁴ Richard D. Robinson, ¹ Rodney S. Ruoff, [#] Sayeef Salahuddin, ² , Jie Shan, ³ Li Shi, ⁰ Michael G. Spencer, ^b Mauricio Terrones, ⁰ Wolfgang Windl, ⁹ and Joshua E. Goldberger. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene, ACS Nano, (03 2013): 0. doi:
01/09/2014	5.00 X. H. Kong, H. X. Ji, R. D. Piner, H. F. Li, C. W. Magnuson, C. Tan, A. Ismach, H. Chou,, and R. S. Ruoff. Non-destructive and rapid evaluation of chemical vapor deposition graphene by darkfield optical microscopy, Appl. Phys. Lett., (05 2013): 0. doi:

TOTAL: 2

Number of Papers published in non peer-reviewed journals: 3

(c) Presentations

- 1. AVS Texas Chapter. University of Texas at Dallas, Dallas, Texas, June 7th 2012.
- 2. 2D Materials Beyond Graphene. Ohio State University, Columbus, Ohio, August 7th-8th 2012. (Partially sponsored by ARO).
- 3. TMS 2013, San Antonio, TX.
- 4. MRS Spring Meeting 2013, San Francisco, CA.

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
01/09/2014	3.00 Ariel Ismach,†,* Harry Chou,† Domingo A. Ferrer,‡ Yaping Wu,§ Stephen McDonnell,^ Herman C. Floresca,^, Alan Covacevich,† Cody Pope,† Richard Piner,† Moon J. Kim,^ Robert M. Wallace,^ Luigi Colombo,, and, Rodney S. Ruoff. Toward the Controlled Synthesis ofHexagonal Boron Nitride Films, ACS Nano (05 2012)
08/27/2012	2.00 first_Ariel last_Ismach, first_Harry last_Chou, first_Domingo A. last_Ferrer, first_Yaping last_Wu, first_Stephen last_McDonnell, first_Herman C. last_Floresca, first_Alán last_Covacevich, first_Cody last_Pope, first_Richard last_Piner, first_Moon J. last_Kim, first_Robert M. last_Wallace, first_Luigi last_Colombo, first_Rodney S. last_Ruoff. Toward the Controlled Synthesis ofHexagonal Boron Nitride Films, ACS Nano (05 2012)
TOTAL:	2

Number of Manuscripts:

Books

<u>Received</u>	<u>Book</u>
TOTAL:	

<u>Received</u>	<u>Book Chapter</u>
TOTAL:	

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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ariel ismach	1.00
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FTE Equivalent: **1.00**

Total Number: **1**

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
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Rodney S Ruoff	1.00	Yes
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FTE Equivalent: **1.00**

Total Number: **1**

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
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Chen Zhang	0.50	materials science
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Alan Covacevich	0.50	materials science
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Cody Pope	0.50	materials science
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FTE Equivalent: **1.50**

Total Number: **3**

⁶
Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Period Covered by Report: 8/1/11 – 7/31/13

Synthesis and Characterization of Hexagonal Boron Nitride (h-BN) Films.

Team members: Postdoc Dr. Ariel Ismach, graduate student Harry Chao; Prof. Rodney S. Ruoff. Also, collaboration with the Sanjay Banerjee group of the ECE Department of UT Austin

Proposal Number: 58313-MS

Agreement Number: W911NF-10-1-0428

Abstract:

The large-area growth of hexagonal boron nitride (h-BN) with controllable thickness (number of layers) and down to the 1-2 layers was demonstrated. In addition to the standard characterization tools used for h-BN films, such as, scanning and transmission electron microscopies (SEM and TEM), Raman spectroscopy and mapping and x-ray photoelectron spectroscopy (XPS), other less common methodologies were used as well. For example; low energy electron microscopy and diffraction was found to provide large-area and accurate number of layers; Time of flight secondary ion mass spectroscopy (TOF-SIMS) provided with a 3D mapping of elements and photoluminescence (PL) measurements were detected even from a 1-2 layers on top of a thin graphite layer, and thus, proving the presence of the h-BN phase on top of the graphene/graphite when being very challenging to do so by means of other methodologies. These results allowed us to study in better detail the growth mechanism and few manuscripts are in preparation. We believe our work will lead to a better understanding of the h-BN growth process and thus pave the way to a wide variety of applications.

The growth of ultra-thin h-BN films was, similar to the case of graphene, pioneered by surface scientists in the 90's^{1, 2} in ultra-high vacuum systems and on single-crystal transition metals. Like the graphene, it has also “resuscitated” and re-tested in LPCVD systems on polycrystalline metal films³ and foils,^{4, 5} which are more affordable and potentially suitable for large-scale production. However, graphene growth studies have several advantages and significant advance has been achieved in the last few years. Thanks to the huge amount of research on graphitic materials in the last decades, a set of reliable and highly efficient characterization tools (Raman spectroscopy being the most prominent)^{6, 7} were developed and applied successfully to characterize the graphene films, number of layers, doping, strain, defects, isotopic labeling, etc. These tools enabled the high throughput characterization of graphene growth needed for the discovery of single-layer graphene growth on polycrystalline copper foils and the elucidation of the surface-mediated- growth mechanism reported for the first time in our group.^{8, 9} The characterization of ultra-thin h-BN films was proven to be more challenging and no fast and reliable method for the

large-scale characterization of such films was reported so far and might be one of the reasons for the lack of understanding of their growth mechanism.

In this report we summarize our studies on the growth of ultra-thin h-BN films in low-pressure chemical vapor systems with hot and cold-wall configurations. Different precursors were studied as well, such as diborane-ammonia and ammonia-borane. The synthesized films were studied by means of scanning and transmission electron microscopy (SEM and TEM), Raman mapping and spectroscopy, optical microscope (OM), scanning tunneling microscope (STM), conducting atomic force microscope (c-AFM), low-energy electron microscopy and diffraction (LEEM and LEED), time of flight secondary ion mass spectroscopy (TOF-SIMS), x-ray photoelectron spectroscopy (XPS) and photoluminescence (PL).

Synthesis

1. Diborane-ammonia ($B_2H_6-NH_3$ - gases): Early results with these precursors were published in 2012.⁵ Briefly, LPCVD growth of h-BN in a hot-wall system under the flow of diborane, ammonia and hydrogen, was optimized for the growth of h-BN films with controllable number of layers, from < 5 to > 100 on Ni foils (based on intensive TEM characterization). Further studies were continued in a cold-wall system with base pressure in the range of $\sim 10^{-9}$ Torr (in contrast to ~ 10 mTorr in the standard LPCVD). Based on knowledge achieved while growing graphene,¹⁰ metal foil enclosures (pockets) were tested as well. These experiments led to the formation of ultra-thin h-BN films (1-3 layers) with many triangular ad-layers (single-crystal). Typical growth was carried out at ~ 1000 °C, on Ni. Figure 1 shows SEM and TEM images of a typical few layer h-BN achieved by this method.

2. Ammonia-borane (H_3NBH_3 -solid): This precursor was used in an LPCVD system with a separated heating device to sublime the ammonia-borane powder at ~ 110 °C while the samples were heated in a tube furnace to ~ 1000 °C. Very interesting results were obtained in Ni enclosures where single-crystal triangular h-BN domains of ~ 100 microns in size were observed, Figure 2 shows SEM and TEM images of a 1-2 layer h-BN on Ni sample.

The characterization of the h-BN films was performed by a wide variety of methodologies, including the common methods to characterize such films, i.e. OM, SEM, TEM, XPS and Raman. Additional less common methodologies were used as well, such as LEED/LEEM, STM, c-AFM, TOF-SIMS and PL measurements. The expanded list of characterization tools allowed for the large-area ($100s\ \mu m^2$) characterization of the number of layers (LEEM/LEED, not possible in h-BN with Raman, Figure 3), the identification of a 1-2 h-BN layers on top of a thin graphite (PL, not possible with Raman due to the overlap between the D band in graphite/graphene and the h-BN signal and due to the cross-section Raman signal of h-BN comparing to that of graphite, Figure 5

and 6). The later results might be the only PL measurements on such ultra-thin h-BN (down to 1-2 layers over large areas proved by LEEM) done so far.

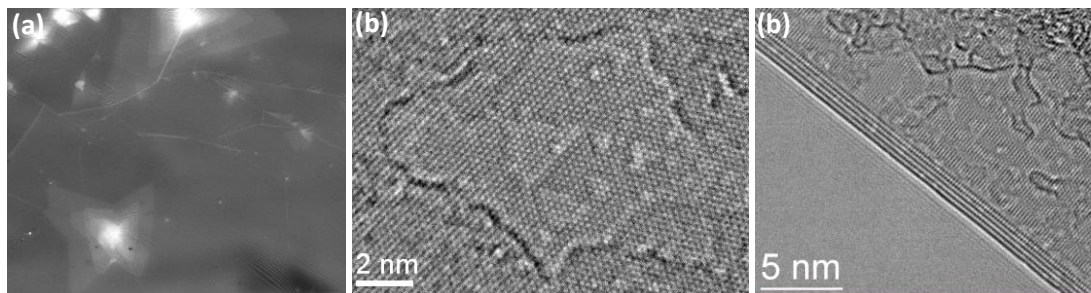


Figure 1: CVD in a cold-wall system with UHV base pressure: (a) SEM of a typical sample showing full coverage, wrinkles and ad-layers. (b)-(c) High resolution TEM images showing the hexagonal lattice with triangular etching pits, (b), and the film edge showing 4 layers, (c).

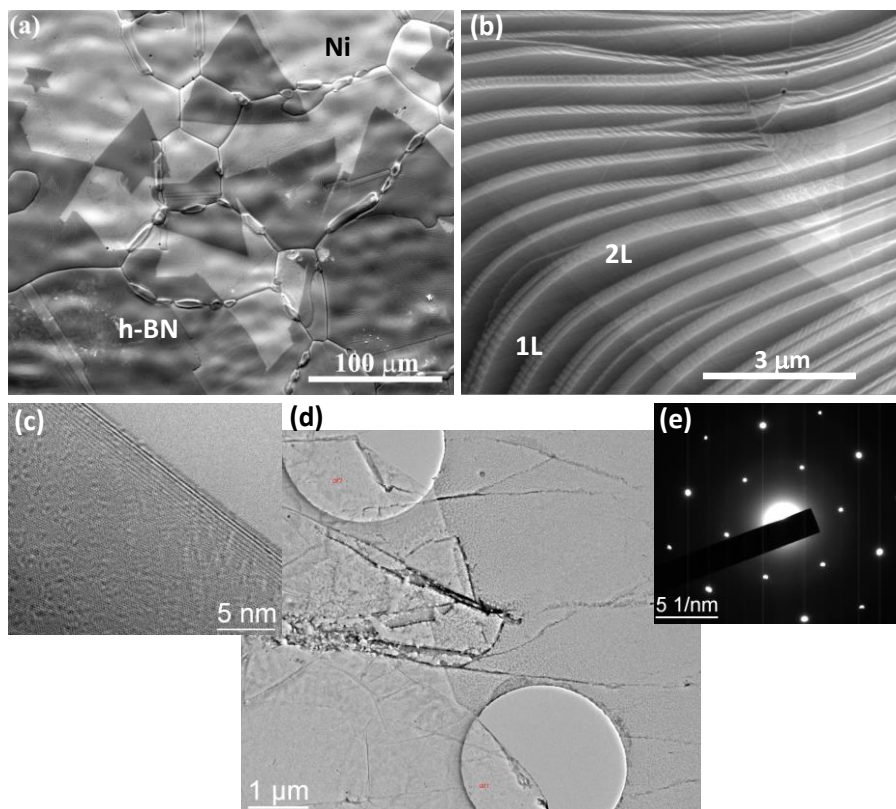


Figure 2: (a) – (b) Scanning electron microscope images showing submonolayer h-BN film on Ni, showing the triangular single-crystal domains as big as ~100 μm. Single-layer h-BN appears dark and the Ni (presumably Ni oxide) bright. (c) – (d) Transmission electron microscope images of a typical 1-2 L h-BN films on a perforated silicon nitride membrane together with the selective area electron diffraction hexagonal pattern in (e).

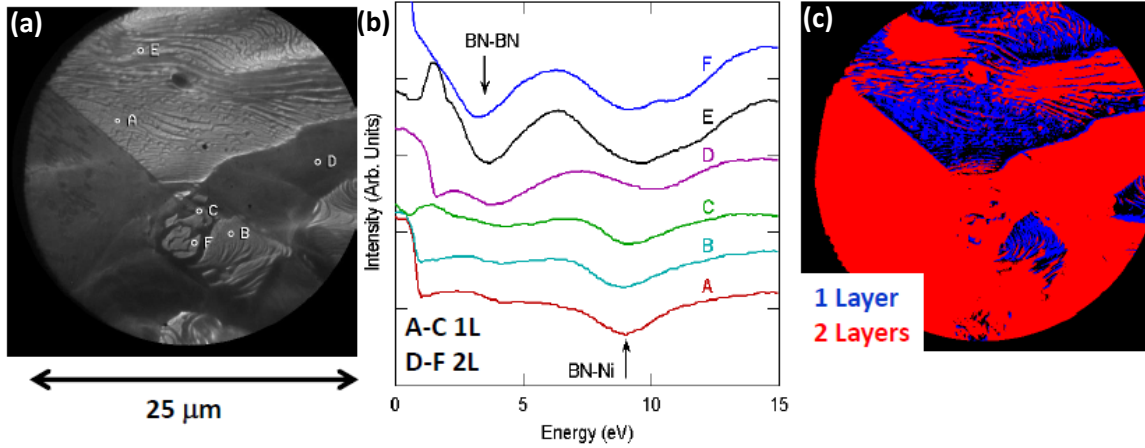


Figure 3: LEEM and LEED characterization of h-BN on Ni. (a) LEEM image of a sample similar to that in Figure 1(a)-(b). (b) Spectra taken at various points in (a). The ‘dips’ in the spectra arising from Ni-BN or BN-BN transitions are labeled. (c) Mapping of the number of layers. This might be the only known methodology for the large-scale characterization of the number of layers in ultra-thin h-BN films.

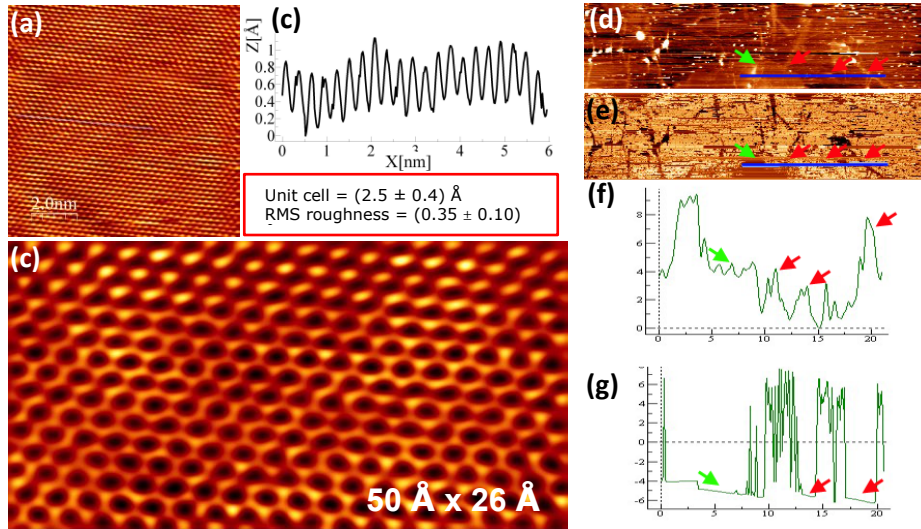


Figure 4: (a) SPM characterization of ultra-thin h-BN films. (a)-(c) High resolution STM of monolayer h-BN on Ni showing the hexagonal lattice. (d) topographic image of a few layer h-BN transferred to Si substrate (e) c-AFM of the same area in (d) showing correlation between the topography (bright=thicker) and conduction in the vertical direction (dark=less conduction), i.e. thicker areas and wrinkles show less conduction as expected. (f) and (g) show the cross section along the blue line in (d) and (e) respectively.

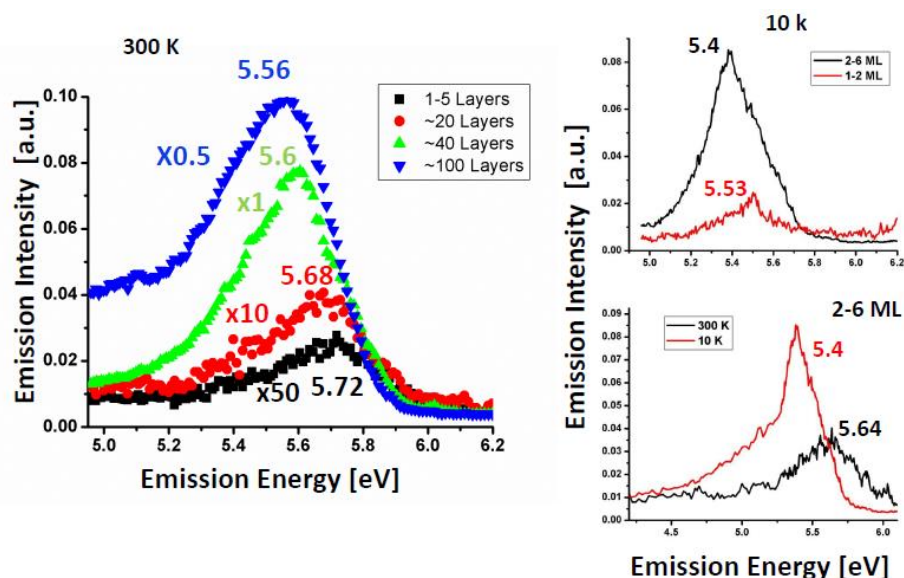


Figure 5: PL measurements: (a) PL signal as a function of the number of layers in the h-BN film at room temperature. (b) PL measurement at 10 K on ultra-thin h-BN films with 2-4 layers (black) and 1-2 layers (red). (c) Comparison between PL signal at 300 K and 10 K for a 2-4 layers film (in collaboration with Dr. Shaul Aloni – LBNL and Prof. Hongxing Jiang – Texas Tech University)

Ongoing Projects:

1. Thermal characterization (in collaboration with Prof. Li Shi – UT Austin).
2. Mechanical characterization (Ruoff group).
3. Optical characterization (in collaboration with Dr. Shaul Aloni – LBNL and Prof. Hongxing Jiang – Texas Tech University).
4. Chemical functionalization such as fluorination of ultra-thin h-BN films (Ruoff group).

References

1. Nagashima, A.; Tejima, N.; Gamou, Y.; Kawai, T.; Oshima, C., ELECTRONIC-STRUCTURE OF MONOLAYER HEXAGONAL BORON-NITRIDE PHYSISORBED ON METAL-SURFACES. *Physical Review Letters* 1995, 75, 3918-3921.
2. Nagashima, A.; Tejima, N.; Gamou, Y.; Kawai, T.; Oshima, C., ELECTRONIC DISPERSION-RELATIONS OF MONOLAYER HEXAGONAL BORON-NITRIDE FORMED ON THE NI(111) SURFACE. *Physical Review B* 1995, 51, 4606-4613.
3. Shi, Y. M.; Hamsen, C.; Jia, X. T.; Kim, K. K.; Reina, A.; Hofmann, M.; Hsu, A. L.; Zhang, K.; Li, H. N.; Juang, Z. Y.; Dresselhaus, M. S.; Li, L. J.; Kong, J., Synthesis of Few-Layer Hexagonal Boron Nitride Thin Film by Chemical Vapor Deposition. *Nano Letters* 2010, 10, 4134-4139.
4. Song, L.; Ci, L.; Lu, H.; Sorokin, P. B.; Jin, C.; Ni, J.; Kvashnin, A. G.; Kvashnin, D. G.; Lou, J.; Yakobson, B. I.; Ajayan, P. M., Large Scale Growth and Characterization of Atomic Hexagonal Boron Nitride Layers. *Nano Letters* 2010, 10, 3209-3215.

5. Ismach, A.; Chou, H.; Ferrer, D. A.; Wu, Y.; McDonnell, S.; Floresca, H. C.; Covacevich, A.; Pope, C.; Piner, R.; Kim, M. J.; Wallace, R. M.; Colombo, L.; Ruoff, R. S., Towards the Controlled Synthesis of Hexagonal Boron Nitride Films. *ACS Nano* 2012, 6, 6378-6385.
6. Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K., Raman spectrum of graphene and graphene layers. *Physical Review Letters* 2006, 97.
7. Dresselhaus, M. S., On the past and present of carbon nanostructures. *Physica Status Solidi B-Basic Solid State Physics* 2011, 248, 1566-1574.
8. Li, X.; Cai, W.; Colombo, L.; Ruoff, R. S., Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling. *Nano Letters* 2009, 9, 4268-4272.
9. Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S., Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* 2009, 324, 1312-1314.
10. Li, X.; Magnuson, C. W.; Venugopal, A.; Tromp, R. M.; Hannon, J. B.; Vogel, E. M.; Colombo, L.; Ruoff, R. S., Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper. *Journal of the American Chemical Society* 2011, 133, 2816-2819.

List of publications under ARO sponsorship during this reporting period.

(a) Papers published in peer-reviewed journals:

1. Ismach, A.; Chou, H.; Ferrer, D. A.; Wu, Y.; McDonnell, S.; Floresca, H. C.; Covacevich, A.; Pope, C.; Piner, R.; Kim, M. J.; Wallace, R. M.; Colombo, L.; Ruoff, R. S., Toward the controlled synthesis of hexagonal boron nitride films. *ACS Nano* **2012**, 6 (7), 6378-85.
2. Butler, Sheneve Z.; Hollen, Shawna M.; Cao, Linyou; Yi Cui, Jay A. Gupta, Humberto R. Gutierrez, Tony F. Heinz, Seung Sae Hong, Jiaxing Huang, Ariel Ismach, Ezekiel Johnston-Halperin, Masaru Kuno, Vladimir V. Plashnitsa, Richard D. Robinson, Rodney S. Ruoff, Sayeef Salahuddin, Jie Shan, Li Shi, Michael G. Spencer, Mauricio Terrones, Wolfgang Windl and Joshua E. Goldberger. Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene . *ACS Nano* **2013**, 7 (4), 2898-2926.
3. X. H. Kong, H. X. Ji, R. D. Piner, H. F. Li, C. W. Magnuson, C. Tan, A. Ismach, H. Chou, and R. S. Ruoff. Non-destructive and rapid evaluation of chemical vapor deposition graphene by dark field optical microscopy. *APPLIED PHYSICS LETTERS* **2013**, 103, 043119.

(b) Manuscripts in Preparation:

1. A. Ismach, H. Chou, *et al.* How hexagonal boron nitride grows?
2. H. Chou, A. Ismach *et al.* Large-scale characterization of 2D layered materials by TOF-SIMS
2. P. C. Mende, A. Ismach, H. Chou, Q. Gao, M. Widom, L. Colombo, R. Ruoff and R. M. Feenstra Characterization of hexagonal boron nitride layers on nickel surfaces

(c) Presentations

1. AVS Texas Chapter. University of Texas at Dallas, Dallas, Texas, June 7th 2012.
2. 2D Materials Beyond Graphene. Ohio State University, Columbus, Ohio, August 7th-8th 2012. (Partially sponsored by ARO).
3. TMS 2013, San Antonio, TX.
4. MRS Spring Meeting 2013, San Francisco, CA.

(d) Student/Supported Personnel Metrics (name, % supported, %Full Time Equivalent (FTE) support provided by this agreement, and total for each category):**1. Graduate Students:**

a. **Harry Chou: 50%-0.50 / 8.3%-0.083**

b. Total = 0.083

2. Post Doctorates:

a. **Ariel Ismach: 100%-1.0 / 66.67%-0.667**

b. Hyung Wook Ha: 100%-1.0 / 16.7%-0.167

c. Total = 0.834

3. Faculty

a. Rodney S. Ruoff: 100%-1.0 / 8.3%-0.083

b. Total = 0.083

4. Undergraduate Students

a. Alan Covacevich: 50%-0.50 / 8.3%-0.083

b. Cody Pope: 50%-0.50 / 16.7%-0.167

c. Nishant Jayant: 50%-0.50 / 8.3%-0.083

d. Chen Zhang: 50%-0.50 / 8.3%-0.083

e. Total = 0.416